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Applicant: Tonen Co., Ltd.

[Title of the Invention]

Production of Metal Dithioxanthates

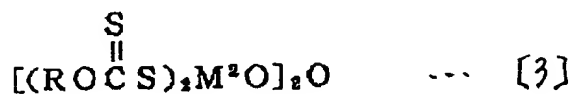
[Abstract]

[Constitution] A process for producing a metal dithioxanthate represented by the general formula  $((\text{ROCS}_2)_2\text{M}^2\text{O})_2\text{O}$  (wherein  $\text{M}^2$  is molybdenum or tungsten; and R has the same meanings as described above), which comprises reacting a dithioxanthate represented by the general formula  $\text{ROCS}_2\text{M}^1$  (wherein  $\text{M}^1$  is an alkaline component; and R has the same meanings as described above) with a molybdate or tungstate in the presence of a mineral acid is provided.

[Effect] Molybdenum dithioxanthates and tungsten dithioxanthates can be obtained efficiently, which have high solubility to mineral oils, and when added to a lubricating oil, exhibit an excellent friction-reducing effect.

[Claims]

[Claim 1] A process for producing a metal dithioxanthate represented by the general formula [3]:



(wherein  $\text{M}^2$  is molybdenum or tungsten; and R is a hydrocarbon group of 1-30 carbons), which comprises reacting a hydroxy-containing compound represented by the general formula [1]:

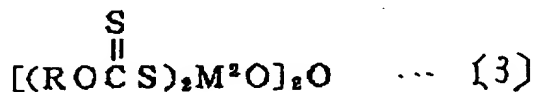


(wherein R has the same meanings as described above) with carbon disulfide and an alkaline component hydroxide in the presence of an oxygen-containing compound having a lower chain hydrocarbon group to give a dithioxanthate represented by the general formula [2]:



(wherein  $\text{M}^1$  is an alkaline component; and R has the same meanings as described above), and then reacting the latter with a molybdate or tungstate in the presence of a mineral acid.

[Claim 2] A process for producing a metal dithioxanthate represented by the general formula [3]:



(wherein  $\text{M}^2$  is molybdenum or tungsten; and R is a hydrocarbon

group of 1-30 carbons), which comprises reacting a dithioxanthate represented by the general formula [2]:



(wherein  $M^1$  is an alkaline component; and R has the same meanings as described above) with a molybdate or tungstate in the presence of a mineral acid.

[Detailed Description of the Invention]

[Industrial Field of Application]

The present invention relates to an improved process for producing metal dithioxanthates. More particularly, the invention relates to a process for producing molybdenum dithioxanthates or tungsten dithioxanthates in a simple operation in high purity and in high yield. These dithioxanthates are useful as additives to lubricating oils since they are soluble well in mineral oils and exhibit a high friction-reducing effect when added to lubricating oil.

[Prior Art]

The molybdenum dithioxanthates having a long chain alkyl group are useful as additives to lubricating oil since they have a high friction-reducing effect when added to the lubricating oil. As a process for producing molybdenum dithioxanthates, for example, a process for producing molybdenum dimethyldithioxanthate  $[(\text{CH}_3\text{OCS}_2)_2\text{MoO})_2\text{O}]$  is known,

in which carbon disulfide is added to a solution of potassium hydroxide in methanol to give potassium methyldithioxanthate ( $\text{CH}_3\text{OCS}_2\text{K}$ ), and sulfur dioxide gas is bubbled into an aqueous solution containing potassium methyldithioxanthate and sodium molybdate to give molybdenum dimethyldithioxanthate (Inorganic Chemistry, vol.6, no.5, 998-1003 (1967)). This process, however, requires a complicated operation, and when a molybdenum dithioxanthate having a long chain alkyl group, for example, molybdenum dioleyldithio-xanthate, is produced according to this process, the product, though readily soluble in lubricating base oil, has only a slight friction-reducing effect in a shell 4-ball test. There was a problem that the measured friction coefficient of a lubricating oil composition containing said product fell far short of that of a commercially available friction-reducing agent, molybdenum oxysulfide dithiocarbamate (MoDTC).

[Problems that the Invention is to Solve]

In this situation, the invention intends to provide a process for producing molybdenum dithioxanthates or tungsten dithioxanthates in a simple operation in high purity and in high yield. These dithioxanthates are useful as additives to lubricating oils since they are soluble well in mineral oils and exhibit a high friction-reducing effect when added to lubricating oil.

[Means for Solving the Problems]

The present inventors worked assiduously to study to achieve the above purpose. As results, they found that the purpose can be accomplished by reacting a hydroxy-containing compound with carbon disulfide and an alkaline component hydroxide in the presence of a specific compound, and then reacting the product with a molybdate or tungstate in the presence of a mineral acid. Thus, the invention was completed based on this finding. Briefly, the invention provides a process for producing a metal dithioxanthate represented by the general formula [3]:



(wherein  $\text{M}^2$  is molybdenum or tungsten; and R is a hydrocarbon group of 1-30 carbons), which comprises reacting a hydroxy-containing compound represented by the general formula [1]:

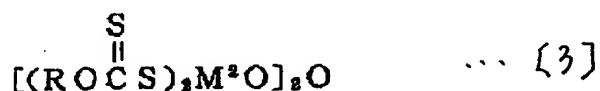


(wherein R has the same meanings as described above) with carbon disulfide and an alkaline component hydroxide in the presence of an oxygen-containing compound having a lower chain hydrocarbon group to give a dithioxanthate represented by the general formula [2]:



(wherein  $\text{M}^1$  is an alkaline component; and R has the same meanings

as described above), and then reacting the latter with a molybdate or tungstate in the presence of a mineral acid. The invention also provides a process for producing a metal dithioxanthate represented by the general formula [3]:



(wherein  $\text{M}^2$  is molybdenum or tungsten; and R is a hydrocarbon group of 1-30 carbons), which comprises reacting a dithioxanthate represented by the general formula [2]:

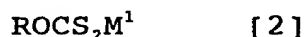


(wherein  $\text{M}^1$  is an alkaline component; and R has the same meanings as described above) with a molybdate or tungstate in the presence of a mineral acid.

The invention will be explained in detail as follows. In the invention, first, a hydroxy-containing compound of the general formula [1]:



(wherein R is a hydrocarbon group of 1-30 carbons) with carbon disulfide and an alkaline component hydroxide to give a dithioxanthate salt of the general formula [2]:



(wherein  $\text{M}^1$  is an alkaline component; and R has the same meanings as described above). In the above-described general formulae

[1] and [2], R is a hydrocarbon group of 1-30 carbons including saturated and unsaturated hydrocarbon group, specifically alkyl group of 1-30 carbons, alkenyl group of 2-30 carbons, cycloalkyl group of 6-30 carbons, aryl group of 6-30 carbons, alkylaryl group of 7-30 carbons, arylalkyl group of 7-30 carbons, and the like. Particularly, the finally produced molybdenum dithioxanthates or tungsten dithioxanthates in which R contains 8-22 carbons have an excellent friction-reducing effect as lubricating oil additives and are preferred accordingly. The hydroxy-containing compounds represented by the general formula [1] includes, for example, methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, pentyl alcohol, hexyl alcohol, and heptyl alcohol, as well as 2-ethylhexyl alcohol, nonyl alcohol, decyl alcohol, lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, eicosyl alcohol, oleyl alcohol, cyclohexyl alcohol, p-t-butylphenol, octylphenol, nonylphenol, and the like. The alkaline component of the invention includes alkali metals and ammonium ion. Accordingly, as the alkaline component hydroxide, for example, lithium hydroxide, potassium hydroxide, sodium hydroxide, ammonium hydroxide, and the like are used.

In the invention, the reaction of the hydroxy-containing compound with carbon disulfide and the alkaline component hydroxide has to be carried out in the presence of an oxygen-containing compound having a lower chain hydrocarbon

group. The oxygen-containing compound having a lower chain hydrocarbon group includes, for example, alcohols, ketones and ethers of 1-10 carbons, preferably 1-5 carbons, more preferably 1 or 2 carbons, specifically, methanol, ethanol, propanol, butanol, acetone, methyl ethyl ketone, dimethyl ether, diethyl ether, dipropyl ether, and the like. These compounds may be used alone or as a mixture of two or more. The oxygen-containing compound raises water solubility of the above-described hydroxy-containing compound to improve its compatibility. The reaction may be carried out as follows. A mixture of the above-described hydroxy-containing compound, a substantially equimolar amount of the alkaline component hydroxide and a slightly excess molar amount of carbon disulfide is allowed to react in the presence of the above-described oxygen-containing compound having a lower chain hydrocarbon group if required in an aqueous medium, preferably at a temperature of 0-70°C for a period of 30 minutes to 20 hours. The oxygen-containing compound may be used usually in an amount of 700-2,000 parts by weight for 100 parts by weight of the hydroxy-containing compound. Thus, the dithioxanthate salt represented by the general formula [2]:

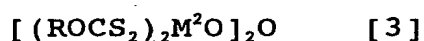


(wherein R and M<sup>1</sup> have the same meanings as described above) can be obtained.

Next, the dithioxanthate salt of the above general



formula [2] is allowed to react with a molybdate or tungstate salt in the presence of a mineral acid. The molybdate or tungstate may be any of anhydride and hydrate, and may be used in a substantially equimolar amount for the dithioxanthate salt of the general formula [2]. The mineral acid includes those having an oxidizing action, for example, nitric acid, sulfuric acid, etc., and may be used alone or as a mixture of two or more. Particularly, preferred is nitric acid. The mineral acid may be used usually in an amount selected from 400-1,000 parts by weight for 100 parts by weight of the molybdate or tungstate (as anhydride). The preferred amount may be in a range of 450-600 parts by weight. Nitric acid may be used usually as 0.5N-2N aqueous solution. The reaction is carried out in an aqueous medium at a temperature of 0-15°C, preferably 2-8°C, for a period of 2-30 hours, preferably 4-10 hours. Thus, the metal dithioxanthate of the general formula [3]:



(wherein  $M^2$  is molybdenum or tungsten; and R has the same meanings as described above) can be obtained.

Specific examples of the metal dithioxanthates having the same chain length hydrocarbon group represented by the above general formula [3] are molybdenum dimethyldithioxanthate, molybdenum diethyldithioxanthate, molybdenum dipropyldithioxanthate, molybdenum dibutyldithioxanthate, molybdenum dipentyldithioxanthate, molybdenum

dihexyldithioxanthate, molybdenum diheptyldithioxanthate, as  
 well as molybdenum di(2-ethylhexyl)dithioxanthate,  
 molybdenum dinonyldithio-xanthate, molybdenum  
 didecyldithioxanthate, molybdenum dilauryldithioxanthate,  
 molybdenum dimyristyldithio-xanthate, molybdenum  
 dipalmityldithioxanthate, molybdenum  
 distearyldithioxanthate, molybdenum dieicosyldithioxanthate,  
 molybdenum dioleyldithio-xanthate, molybdenum  
 dicyclohexyldithioxanthate, molybdenum di(p-t-  
 butylphenyl)dithioxanthate, molybdenum  
 di(octylphenyl)dithioxanthate, molybdenum  
 di(nonylphenyl)dithio-xanthate, and the like, and the  
 corresponding tungsten salts. The molybdenum dithioxanthates  
 or tungsten dithioxanthates of the above general formula [3]  
 obtained in the invention, when added to lubricating oil,  
 exhibit an excellent friction-reducing effect.

#### Examples

The invention will be explained in more detail by the  
 following examples, which are not intended to limit the  
 invention.

#### Example 1

To a mixture of 26 g of 2-ethylhexyl alcohol and 16 g  
 of 50wt% sodium hydroxide aqueous solution were added 150 g  
 of methanol and 200 g of water, and further 16 g of carbon  
 disulfide. The mixture was allowed to react for 5 hours while

keeping at 10°C to give a red jelly-like product. To this product was added an aqueous solution of 48.4 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 200 g of water, and further 300 g of 1N-nitric acid aqueous solution. The mixture was allowed to react at 5°C for 6 hours to give a blue reaction mixture of which the upper layer was oil. To this mixture was then added 500 g of toluene, and the mixture was filtered and washed with water to give a solid product. This solid product contained 95wt% or more of molybdenum di(2-ethyl-hexyl)dithioxanthate as Mo.

#### Example 2

To a mixture of 37.2 g of lauryl alcohol and 16 g of 50wt% sodium hydroxide aqueous solution were added 600 g of methanol and 500 g of water, and further 16 g of carbon disulfide. The mixture was allowed to react at 40-50°C for 5 hours to give a red solid product. To this product was added an aqueous solution of 48.4 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 200 g of water, and further 300 g of 1N-nitric acid aqueous solution. The mixture was allowed to react at 5°C for 6 hours to give a blue reaction mixture of which the upper layer was oil. To this mixture was then added 500 g of toluene, and the mixture was filtered and washed with water to give a solid product. This solid product contained 95wt% or more of molybdenum dilauryldithioxanthate as Mo.

### Example 3

To a mixture of 26.8 g of oleyl alcohol and 8 g of 50wt% sodium hydroxide aqueous solution were added 300 g of methanol, and further 8 g of carbon disulfide. The mixture was allowed to react at 10°C for 5 hours to give a red clear solution. To this solution was added an aqueous solution of 24.2 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 100 g of water to yield yellow crystals as precipitate. This was dissolved with addition of 200 g of water, to which was added 150 g of 1N-nitric acid aqueous solution. The mixture was allowed to react at 5°C for 6 hours to give a blue reaction mixture of which the upper layer was oil. To this solution was then added 500 g of toluene, and the toluene layer was collected and evaporated to give a product. This product contained 98wt% or more of molybdenum dioleyldithioxanthate as Mo.

### Example 4

To a mixture of 26.8 g of oleyl alcohol and 8 g of 50wt% sodium hydroxide aqueous solution were added 200 g of acetone and 100 g of water, and further 8 g of carbon disulfide. The mixture was allowed to react at 10°C for 6 hours to give a red clear solution. To this solution was added an aqueous solution of 24.2 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 50 g of water, and further 200 g of 1N-nitric acid aqueous solution. The mixture was allowed to react at 5°C for 6 hours to give a blue reaction mixture of which the upper layer was oil. To this

solution was then added 500 g of toluene, and the toluene layer was collected and evaporated to give a product. This product contained 95wt% or more of molybdenum dioleyldithioxanthate as Mo.

#### Example 5

To a mixture of 26.8 g of oleyl alcohol and 8 g of 50wt% sodium hydroxide aqueous solution were added 100 g of t-butanol and 100 g of water, and further 8 g of carbon disulfide. The mixture was allowed to react at 10°C for 5 hours to give a red clear solution. To this solution was added an aqueous solution of 24.2 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 50 g of water, and further 100 g of 1N-nitric acid aqueous solution. The mixture was allowed to react at 5°C for 6 hours to give a light blue reaction mixture of which the upper layer was oil. To this solution was then added 500 g of toluene, and the toluene layer was collected and evaporated to give a product. This product contained 95wt% or more of molybdenum dioleyldithioxanthate as Mo.

#### Example 6

To a mixture of 26.8 g of oleyl alcohol and 8 g of 50wt% sodium hydroxide aqueous solution were added 300 g of methanol, and further 8 g of carbon disulfide. The mixture was allowed to react for 5 hours while keeping at 10°C to give a yellow clear liquid product. To this product was added an aqueous solution of tungsten ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) (48.5 g dissolved in 100 g

of water), and further 200 g of water to dissolve the crystals. After addition of 300 g of 1N-nitric acid aqueous solution, the mixture was allowed to react at 5°C for 6 hours. Thus, the reaction mixture of which the upper layer was oil was obtained. To this solution was then added 500 g of toluene, and the toluene layer was collected and evaporated to give a solid product. This product contained 95wt% or more of tungsten dioleyldithio-xanthate as Wo.

#### Comparative Example 1

To a mixture of 26.8 g of oleyl alcohol and 8 g of 50wt% sodium hydroxide aqueous solution were added 300 g of toluene and 100 g of methanol, and further 8 g of carbon disulfide. The mixture was allowed to react at 10°C for 5 hours to give a red clear solution. To this solution was added an aqueous solution of 24.2 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 100 g of water, and further 150 g of 1N-nitric acid aqueous solution. The mixture was allowed to react at 5°C for 1.5 hours to give a blue reaction mixture of which the upper layer was oil. To this solution was then added 500 g of toluene, and the toluene layer was collected and evaporated to give a product. This product contained 80wt% of molybdenum dioleyldithioxanthate as Mo.

#### Comparative Example 2

To a mixture of 26.8 g of oleyl alcohol and 8 g of 50wt% sodium hydroxide aqueous solution were added 100 g of water

and 8 g of carbon disulfide. The mixture was allowed to react at 10°C for 5 hours to give a red clear solution of which the upper layer contained yellow blocks. To this solution was added an aqueous solution of 24.2 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 100 g of water, and further 150 g of 1N-nitric acid aqueous solution. The mixture was allowed to react at 5°C for 1.5 hours to give a reaction mixture containing yellow precipitate. This mixture was filtered and washed with water to give a solid product. This product contained 80wt% of molybdenum dioleyldithioxanthate as Mo.

#### Comparative Example 3

To a mixture of 26.8 g of oleyl alcohol and 8 g of 50wt% sodium hydroxide aqueous solution were added 300 g of methanol and 8 g of carbon disulfide. The mixture was allowed to react at 10°C for 5 hours to give a red clear solution. To this solution was added an aqueous solution of 24.2 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 100 g of water to yield yellow crystals as precipitate. This was dissolved with addition of 200 g of water, and the mixture was allowed to react at 5°C for 1.5 hours while bubbling sulfur dioxide gas to give a blue reaction mixture of which the upper layer was oil. To this solution was then added 500 g of toluene, and the toluene layer was collected and evaporated to give a product. This product contained 80wt% of molybdenum dioleyldithioxanthate as Mo.

#### Comparative Example 4

To a mixture of 26.8 g of oleyl alcohol and 8 g of 50wt% sodium hydroxide aqueous solution were added 100 g of methanol and 100 g of water, and further 8 g of carbon disulfide. The mixture was allowed to react at 10°C for 5 hours to give a red clear solution. To this solution was added an aqueous solution of 24.2 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 100 g of water. The mixture was allowed to react at 5°C for 1.5 hours while bubbling sulfur dioxide gas to give a blue reaction mixture of which the upper layer was oil. To this solution was then added 500 g of toluene, and the toluene layer was collected and evaporated to give a product. This product contained 80wt% of molybdenum dioleyldithioxanthate as Mo.

#### Test 1

A lubricating oil composition comprising mineral oil 100SN as lubricating base oil, 4.0wt% of viscosity index improver of polymethacrylate type, 3.0 wt% of ashless cleaner dispersant of succinimide type, 0.75wt% of anti-wear additive of zinc thiophosphate type, and a friction-reducing agent of which the kind and the amount are shown in Table 1, was prepared. This composition was subjected to a shell 4-ball test at a load of 40 kgf or 20 kgf, revolution number of 1800rpm, and an oil temperature of 90°C for 30 minutes to determine the diameter of wear marks, friction coefficient, and average roughness on the upper ball surface. The results are shown in Table 1. In Table 1, the reaction step (1) indicates the reaction with



carbon disulfide, and the reaction step (2) indicates the reaction with sodium molybdate.

[Table 1]

Table 1-1

| Test No | Friction-Reducing Agent |                                       |                              |  |                     |
|---------|-------------------------|---------------------------------------|------------------------------|--|---------------------|
|         | Type                    |                                       | Reaction step (1)<br>Solvent | Reaction step (2)<br>Addition of HNO <sub>3</sub><br>or<br>bubbling of SO <sub>2</sub> | Amount added<br>ppm |
| 1       | Example 1               | Di (2-ethylhexyl) MoDTX               | Methanol Water               | Addition of HNO <sub>3</sub>   | 230<br>(Mo)         |
| 2       | Example 2               | Dilauryl MoDTX                        | Methanol Water               | Addition of HNO <sub>3</sub>   | 230<br>(Mo)         |
| 3       | Example 3               | Dioleyl MoDTX                         | Methanol                     | Addition of HNO <sub>3</sub>   | 230<br>(Mo)         |
| 4       | Example 4               | Dioleyl MoDTX                         | Acetone Water                | Addition of HNO <sub>3</sub>   | 230<br>(Mo)         |
| 5       | Example 5               | Dioleyl MoDTX                         | t-Butanol Water              | Addition of HNO <sub>3</sub>   | 230<br>(Mo)         |
| 6       | Example 6               | Dioleyl WDTX                          | Methanol                     | Addition of HNO <sub>3</sub>   | 460<br>(W)          |
| 7       | Comparative Example 1   | Dioleyl WDTX                          | Toluene Methanol             | Addition of HNO <sub>3</sub>   | 230<br>(Mo)         |
| 8       | Comparative Example 2   | Dioleyl MoDTX                         | Water                        | Addition of HNO <sub>3</sub>   | 230<br>(Mo)         |
| 9       | Comparative Example 3   | Dioleyl MoDTX                         | Methanol                     | Buddling of SO <sub>2</sub>  | 230<br>(Mo)         |
| 10      | Comparative Example 4   | Dioleyl MoDTX                         | Methanol Water               | Buddling of SO <sub>2</sub>  | 230<br>(Mo)         |
| 11      | —                       | No addition                           | —                            | —  | —                   |
| 12      | —                       | C <sub>8</sub> ~C <sub>13</sub> MoDTC | —                            | —  | 230<br>(Mo)         |

Remark: C<sub>8</sub>-C<sub>13</sub> MoDTC: Molybdenum oxysulfide dithio-carbamate of which the alkyl is of 8-13 carbons (commercially available)

Di(2-ethylhexyl)MoDTX: Molybdenum di(2-ethylhexyl)-dithioxanthate

Dilauryl MoDTX: Molybdenum dilauryldithioxanthate

Dioleyl MoDTX: Molybdenum diolelyldithioxanthate

[Table 2]

Table 1-2

| Test No | Shell 4-Ball Test       |                      |   |                         |                      |   |
|---------|-------------------------|----------------------|---|-------------------------|----------------------|---|
|         | Load 40 kgf             |                      |   | Load 20 kgf             |                      |   |
|         | Wear mark diameter (mm) | Friction coefficient | Average roughness on the upper surface ( $\mu$ m) | Wear mark diameter (mm) | Friction coefficient | Average roughness on the upper surface ( $\mu$ m) |
| 1       | 0.29                    | 0.054                | 0.110   | —                       | —                    | —   |
| 2       | 0.27                    | 0.054                | 0.120   | —                       | —                    | —   |
| 3       | 0.55                    | 0.063                | 0.186   | 0.32                    | 0.051                | 0.107   |
| 4       | 0.59                    | 0.056                | —   | —                       | —                    | —   |
| 5       | 0.53                    | 0.065                | —   | —                       | —                    | —   |
| 6       | 0.58                    | 0.070                | —   | 0.31                    | 0.085                | —   |
| 7       | 1.67                    | 0.094                | —   | —                       | —                    | —   |
| 8       | 1.81                    | 0.084                | —   | —                       | —                    | —   |
| 9       | 0.56                    | 0.098                | 0.216   | —                       | —                    | —   |
| 10      | 0.56                    | 0.099                | 0.234   | —                       | —                    | —   |
| 11      | 0.52                    | 0.113                | 0.579   | 0.33                    | 0.097                | 0.142   |
| 12      | 0.58                    | 0.067                | 0.286   | 0.31                    | 0.063                | 0.156   |

[Advantage of the Invention]

According to the invention, a process for producing molybdenum dithioxanthates or tungsten dithioxanthates in a simple operation in high purity and in high yield is provided. These dithioxanthates are useful as additives to lubricating oils since they are soluble well in mineral oils and exhibit a high friction-reducing effect when added to lubricating oil.